

II. Related Art

Solid, high energy compositions such as rocket propellants, gas generators, explosives, and the like, generally contain particulate solids in the form of oxidizers, fuels, burning rate modifiers, solid explosives, etc., dispersed in elastomeric binders. The elastomeric binders themselves may contain inert polymer materials, but these compositions may also contain high energy, hazards sensitive plasticizers, such as nitrate esters. These plasticizing materials are known to enhance the mechanical properties as well as the energy output of the overall composition. The typical ratio, by weight of plasticizer to total polymer (including prepolymers, crosslinkers and curatives) in binder materials (commonly known as the Pl:Po ratio) is about 2-4, i.e., 2 to 4 parts of energetic plasticizer to one part of polymer in the binder.

Recently, more stringent requirements imposed for lower hazards sensitivity have led to an increased demand for lower energy, but not entirely inert, binders which have become known as reduced energy or intermediate energy binders. The general approach to developing these binders has been to replace or dilute very high energy plasticizers with lower energy plasticizers while holding the Pl:Po ratio substantially constant at about 2-4.

An alternative approach to this problem which seemed logical was to simply dilute the high energy plasticizers with additional binder polymer material to reduce the overall binder energy as this would provide a more dense polymeric network which, in turn, would be expected to be a great deal tougher and more resistant to physical damage, another critical consideration for reducing hazards sensitivity. It was found, however, that at the resultant lower Pl:Po ratios, the lower fraction of plasticizer was insufficient to properly plasticize the binder polymer and this resulted in unsatisfactory mechanical properties, especially with regard to low elongation. Thus, there has remained a need to solve the problem of fully plasticizing the binder polymer at lower Pl:Po ratios to reduce hazards

sensitivity in a manner which preserves good mechanical properties or even enables improvements in mechanical properties.

Crosslinked binders disclosed by Baczuk et al (U.S. Patent 4,386,978) include urethane rubber materials that include certain polyester diols which contain both aliphatic and aromatic ester functions. These are combined with a poly-functional isocyanate having an NCO (isocyanate) functionality of at least 3. Energetic plasticizers are not reduced, however.

Godsey et al (U.S. Patent 5,468,311) discloses a composition having a binder system that includes polyols which may be polyesters or polyethers having a molecular weight from about 400 to about 4,000 and hydroxyl functionalities from about 2.0 to about 2.8. The preferred polyol is polyethylene glycol adipate. The preferred molecular weight range is from about 2,000 to about 3,000. A further patent to Godsey (U.S. Patent 4,298,411) depicts a propellant system that includes a pre-polymer of a hydroxy-terminated polyester and an isocyanate used in very small amounts as a crosslinking agent.

In U. S. Patent 4,775,432 to Kolonko et al, it has further been proposed to use relatively high molecular weight poly(caprolactone) polymers in propellant binders. Those formulae, however, require a ratio of plasticizer to binder that is at least 2.0:1 and preferably at least 2.5:1.

Whereas each of the above references addresses certain previous drawbacks in the art, none predict a low cost, reduced hazards energetic formulation with desired mechanical properties.

Accordingly, it is a primary object of this invention to provide an improved binder system for energetic compositions which maintains excellent mechanical properties, together with reduced hazards sensitivity.

A further object of the invention is to replace an amount of energetic plasticizers in binders for energetic

compositions with binder polymers without sacrificing good mechanical properties.

It is another object of this invention to provide an improved binder system for high energy compositions using high molecular weight polyester prepolymers combined with a relatively low level of energetic plasticizer.

Yet another object of this invention is to provide lower cost energetic compositions of reduced hazards sensitivity and desirable mechanical characteristics.

10 A still further object of this invention is to provide an improved binder system for high energy compositions utilizing isocyanate crosslinked or cured, relatively high molecular weight PTMA pre-polymer as the binder polymer.

Yet still another object of the invention is to
15 provide lower cost energetic materials by replacing part or
all of the RDX or HMX fraction with a suitable solid
material combination such as AP and aluminum.

Other objects and advantages will become apparent to those skilled in the art upon becoming familiar with the descriptions and accounts contained herein together with the appended claims.

SUMMARY OF THE INVENTION

The present invention overcomes many drawbacks in prior energetic compositions by the provision of improved reduced energy binder compositions for solid, high energy formulations including propellants, explosives, gas generators and related materials, together with formulations using these binders. The binders of the invention are particularly advantageous because they are relatively low cost and exhibit improved hazards properties relative to similar, higher energy binders. In addition, the binders promote excellent mechanical properties which allow additional composition variation leeway which, in turn, can be used to reduce cost and hazards sensitivity still further. The excellent mechanical properties survive in the formulations even without the reinforcement of fine particle size nitramines such as HMX and RDX.

The binders are useful with any commonly used solid energetic species and successfully employ binder polymer materials to replace at least part of the energetic plasticizers thereby reducing the levels of energetic plasticizers, particularly nitrate esters, required in the binder. The binder system of the invention succeeds mechanically at levels of energetic plasticizers that are quite low.

The invention accomplishes the foregoing advantages by providing unique binder compositions that employ a cured high molecular weight polyester matrix, particularly polyester polyols which readily undergo crosslinking curing through active hydroxyl group sites using polyisocyanates in combinations with relatively low levels of energetic plasticizers. The preferred embodiment uses high molecular weight poly(tetramethylene adipate) or PTMA with NG, but other energetic plasticizers such as *n*-butyl-2-nitratoethyl nitramine (BuNENA), trimethylolethane trinitrate (TMETN), triethyleneglycol dinitrate (TEGDN), butanetriol trinitrate (BTTN) and other materials also function effectively.

The polyester prepolymer materials of the invention are compounds that are readily plasticized by energetic plasticizers including nitrate ester compounds such that the relative level of high energy plasticizer can be reduced significantly. The formulas make use of material that is sufficiently plasticized at low Pl:Po ratios of about 1.0 such that lower hazards sensitivity advantages associated with the higher relative polymer levels can be taken. It has been found, for example, that PTMA of a rather high molecular weight (MW ~ 6,000 in which the MW is a number average molecular weight) works extremely well. When used with NG at an approximate ratio of 1:1, or even slightly less, the polymer is sufficiently plasticized to enable excellent or superior mechanical properties to be realized.

While the detailed description focuses on the use of PTMA, it is believed that other high molecular weight

polyester polyol materials having sufficient reactive hydroxyl group sites to react with a crosslinking agent, particularly a polyisocyanate, to form a cured polymer matrix may behave similarly. Thus, linear and moderately
5 branched polyester polyols derived from aliphatic and/or aromatic starting materials, or from polymerizable lactones or mixtures thereof of sufficient molecular weight may function in a similar manner. Examples of other such compounds include poly(1,4-butanediol azelate),
10 poly(diethyleneglycol adipate), poly(1,6-hexanediol adipate), poly(1,3-butanediol adipate), etc.

The present invention also provides reduced or intermediate energy binder propellant systems of reduced cost and reduced hazards sensitivity which maintain
15 superior mechanical properties. Some formulas reduce both cost and hazards sensitivity by reducing or eliminating RDX or HMX and further reduce hazards sensitivity by utilizing novel, reduced energy binders. In this manner, it has been found, for example, that some or all of the high priced
20 components RDX or HMX can be replaced by less expensive AP oxidizer and aluminum or other solids combinations.

In one example, a 75% solids propellant was prepared which utilized 53% unground (200 μ) ammonium perchlorate and 22% aluminum (30 μ). That formula also contained 11.3% PTMA
25 of MW approximately 6,200 and 12.19% NG. The propellant gave outstanding mechanical properties and less than 69 cards in NOL card gap testing.

According to the invention, it has also been found that a combination of plasticizers may be used in such
30 formulas including amounts of inert materials to provide further flexibility in formulating useful mixes. An example of such an inert plasticizer is triacetin (TA) or triacetyl glycerine. The use of amounts of inert plasticizer allows a further reduction in the required
35 amount of energetic plasticizer. The percentage of inert plasticizer used may vary greatly in the binder, which itself may vary greatly in the mix. One successful formula

used about 2.5% TA and another about 1.4% TA.

As a general comment with respect to many of the ingredients used in the several exemplary formulae disclosed herein, the following is a partial list of
5 ingredient functions in the energetic compositions:

NC - crosslinker
PTMA - prepolymer
N-100, DDI, IPDI - isocyanate curatives
NG, TMETN, BuNENA, etc. - energetic plasticizers
10 TA - inert plasticizer
2-NDPA, MNA - stabilizers
AP - oxidizer, burn rate modifier
NaNO₃ - oxidizer, chloride scavenger
DCDA - burn rate suppressant
15 Al - fuel
TPB - cure catalyst

It is expected that a range of molecular weights for the PTMA binder material may be successfully used; however, it has been discovered that using molecular weights that
20 are higher produces surprisingly superior results at low Pl:Po ratios. With PTMA, it is believed that the preferred range of molecular weights of PTMA begins above about 4,000 and preferably above 5,000, material of approximately 6,000 MW or greater is most preferred being found highly
25 successful. The material has allowed the formulation of low-binder-energy propellant that requires no HMX or RDX and so can be made out of lower cost materials.

Another important advantageous characteristic of the binders of the invention is a relatively high electrical
30 conductivity. This is also important with respect to reducing hazards by assisting in preventing the accumulation or buildup of large static charges in the associated energetic compositions.

DETAILED DESCRIPTION

35 The goals of the energetic formulae or compositions of the present invention are to reduce cost and reduce hazards

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Baseline reduced-binder-energy formulation

Baseline reduced-binder-energy formulation			
	Ingredient	Weight %	
5	RS 5 sec NC	0.06	Percent Solids
	PTMA 6000	11.30	P1:Po
	N-100	0.97	Hex _B (cal/g)
	NG	12.19	NC/PTMA
	2-NDPA (2-nitrodiphenylamine)	0.12	NCO/OH
10	MNA (N-methyl-p-nitroaniline)	0.36	theor. I ⁰ _{sps} (lb _f s/lb _m)
	AP (200μ)	53.00	theor. ρ (g/cc)
	Al (30μ)	22.00	theor. flame T (°K)
	TPB	(0.01)	

TABLE II

	One-pint-mix properties of baseline reduced-binder-energy formulation (using all 200μ AP, except as noted).		
5	Tensile properties @ 2 in/min, 77°F		
	σ _m (psi)	84	
	ε _m (%)	244	
	ε _r (%)	244	
10	E ₀ (psi)	1610	
	120°F viscosity (kP)		
	η _{0.36}	7	
	η _{0.008}	12	
	120°F pot life (hr)	~27-36	
15	Ballistic properties (with 50/50 90μ/200μ AP)		
	70-g motor r ₁₀₀₀ (in/s)	0.41	
	70-g motor n	0.3	
	CIV (ft/s)	806	
	NOL card gap		
20	1 no-go at 69 cards		
	Hazards sensitivity		
		uncured	cured
25	impact (cm)	6.9	21
	friction (lb _f @ ft/s)	40 @ 8	100 @ 8
	ESD (J)	0.15	0.26
	FJAI (°C)	>300	>300

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TABLE III

Reduced-binder-energy formulation with BuNENA/TA plasticizer			
	Ingredient	Weight %	
	RS 5 sec NC	0.04	Percent Solids 84
5	PTMA 6000	7.23	P1:Po 1.00
	N-100	0.62	Hex _B (cal/g) -850
	BuNENA	6.47	NC/PTMA 0.005
	TA	1.41	NCO/OH 1.3
	MNA	0.23	theor. I ⁰ _{sps} (lb _f s/lb _m) 261.0
10	AP (20μ)	5	theor. ρ (g/cc) 1.85
	AP (200μ)	20	theor. flame T (°K) 3712
	AP (400μ)	35	
	Al (30μ)	22	
15	DCDA (dicyandiamide) (<10μ)	2	
	TPB	(0.01)	

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TABLE IV

One-pint-mix properties of reduced-binder-energy formulation using BuNENA/TA plasticizer.			
5	Tensile properties @ 2 in/min, 77°F		
	σ_m (psi)	104	
10	ϵ_m (%)	174	
	ϵ_r (%)	176	
	E_0 (psi)	2350	
	120°F viscosity (kP)		
	$\eta_{0.36}$	10	
	$\eta_{0.008}$	29	

TABLE V

Reduced-binder-energy formulation with mixed NG/TA plasticizer			
Ingredient		Weight %	
RS 5 sec NC		0.05	Percent Solids 75
PTMA 6000		9.88	P1:Po 1.26
N-100		0.67	Hex _B (cal/g) -100
20	DDI (dimeryl diisocyanate)	0.26	NC/PTMA 0.005
	NG	11.24	NCO/OH 1.3
	TA	2.46	theor. I^0_{sps} (lb _f s/lb _m) 259.7
25	2-NDPA	0.11	theor. ρ (g/cc) 1.83
	MNA	0.33	theor. flame T (°K) 3728
	AP (20 μ)	8	
	AP (400 μ)	45	
	Al (30 μ)	22	
	TPB	(0.01)	

TABLE VI

One-gallon-mix properties of reduced-binder-energy formulation using mixed NG/TA plasticizer.		
5	Tensile properties @ 2 in/min, 77°F	
	σ_m (psi)	79
	ϵ_m (%)	350
	ϵ_r (%)	352
	E_0 (psi)	799
10	120°F viscosity (kP)	
	$\eta_{0.36}$	3
	$\eta_{0.008}$	5
15	120°F pot life (hr)	48
	Ballistic properties (one-pound motors)	
	r_{1000} (in/s)	0.353
	n	0.29

EXAMPLE 3

Another propellant formula which produced excellent mechanical properties is shown in Table V and the one-gallon-mix properties are shown in Table VI. This formula uses an amount of TA along with the NG as plasticizers.

EXAMPLE 4

The formula of this example is shown in Table VII and illustrates a propellant formula that is plasticized with TMETN. This formulation also exhibits excellent mechanical and processing properties as shown in Table VIII.

EXAMPLE 5

The formula and mechanical properties of this example can be seen in Tables IX and X, respectively. In this

example, a substantial fraction of the AP oxidizer has been replaced by NaNO_3 . As with the mixes of previous examples, the mechanical and processing properties were excellent. This mix was also tested for volume resistivity.

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TABLE VII

Reduced-binder-energy formulation with TMETN plasticizer			
	Ingredient	Weight %	
	RS 5 sec NC	0.06	Percent Solids 75
	PTMA 6000	11.34	P1:Po 1.00
10	N-100	0.78	Hex _B (cal/g) -260
	IPDI	0.11	NC/PTMA 0.005
	TMETN	12.32	NCO/OH 1.3
	2-NDPA	0.03	theor. I_{sps}^0 (lb _f s/lb _m) 261.0
	MNA	0.36	theor. ρ (g/cc) 1.82
15	AP (20 μ)	10	theor. flame T (°K) 3663
	AP (200 μ)	43	
	Al (30 μ)	22	
	TPB	(0.01)	

One-pint-mix properties of reduced-binder-energy formulation using TMETN plasticizer.

5	Tensile properties @ 2 in/min, 77°F	
	σ_m (psi)	134
	ϵ_m (%)	338
	ϵ_r (%)	340
	E_0 (psi)	1080
	120°F viscosity (kP)	
	$\eta_{0.36}$	4
	$\eta_{0.008}$	6
	120°F pot life (hr)	
	50-53	

TABLE IX

Reduced-binder-energy formulation with AP, Al, and NaNO ₃ solids			
	Ingredient	Weight %	
	RS 5 sec NC	0.06	Percent Solid 74.75
5	PTMA 6000	11.42	P1:Po 0.99
	N-100	0.98	Hex _B (cal/g) 0
	NG	12.31	NC/PTMA 0.005
	2-NDPA	0.12	NCO/OH 1.3
	MNA	0.36	theor. I ⁰ _{sps} (lb _f s/lb _m) 245.7
10	AP (5μ)	13	theor. ρ (g/cc) 1.89
	AP (70μ)	17	theor. flame T (°K) 3732
	Al (30μ)	23	
	NaNO ₃ (<70μ)	21.75	
	TPB	(0.01)	

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TABLE X

One-gallon-mix properties of reduced-binder-energy formulation using AP, Al, and NaNO ₃ solids.		
5	Tensile properties @ 2 in/min, 77°F	
	σ_m (psi)	244
	ϵ_m (%)	394
	ϵ_r (%)	394
10	E_0 (psi)	1570
	120°F viscosity (kP)	
	$\eta_{0.36}$	7
	$\eta_{0.008}$	23
	120°F pot life (hr)	>35
15	volume resistivity (ohm-cm)	1×10^8

This invention has been described herein in considerable detail in order to comply with the Patent Statutes and to provide those skilled in the art with the information needed to apply the novel principles and to construct and use embodiments as required. However, it is to be understood that the invention can be carried out by specifically different formulas and devices and that various modifications can be accomplished without departing from the scope of the invention itself.

25 What is claimed is: